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(54) Surface-modified pyrogenically produced mixed oxides

(57) Surface-modified, pyrogenically produced mixed oxides which contain two or more components from the series comprising SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , Fe_2O_3 , Nb_2O_5 , V_2O_5 , WO_3 , SnO_2 , GeO_2 and were surface-modified with one or more compounds from the following groups:

Organosilanes of the types

- (a) $(\text{RO})_3\text{Si}(\text{C}_n\text{H}_{2n+1})$,
- (b) $\text{R}'_x(\text{RO})_y\text{Si}(\text{C}_n\text{H}_{2n+1})$,
- (c) $\text{X}_3\text{Si}(\text{C}_n\text{H}_{2n+1})$,
- (d) $\text{X}_2(\text{R}')\text{Si}(\text{C}_n\text{H}_{2n+1})$,
- (e) $\text{X}(\text{R}')_2\text{Si}(\text{C}_n\text{H}_{2n+1})$,
- (f) $(\text{RO})_3\text{Si}(\text{CH}_2)_m\text{-R}'$,
- (g) $(\text{R}')_x(\text{RO})_y\text{Si}(\text{CH}_2)_m\text{-R}'$,
- (h) $\text{X}_3\text{Si}(\text{CH}_2)_m\text{-R}'$,
- (i) $(\text{R})\text{X}_2\text{Si}(\text{CH}_2)_m\text{-R}'$,
- (j) $(\text{R})_2\text{X Si}(\text{CH}_2)_m\text{-R}'$
- (k) Silazanes of the type $\text{R}'\text{R}_2\text{Si-N-SiR}_2\text{R}'$,

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- (l) Cyclic polysiloxanes,
- (m) Polysiloxanes and silicone oils.

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Surface-modified, pyrogenically produced mixed oxides,
5 a process for their preparation and the use thereof

The invention relates to surface-modified, pyrogenically produced mixed oxides, the process for their preparation and the use thereof.

10

The invention provides surface-modified, pyrogenically produced mixed oxides which contain two or more components from the series comprising SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , Fe_2O_3 , Nb_2O_5 , V_2O_5 , WO_3 , SnO_2 , GeO_2 and were surface-modified with
15 one or more compounds from the following groups:

(a) Organosilanes of the type $(\text{RO})_3\text{Si}(\text{C}_n\text{H}_{2n+1})$

R = alkyl, such as, for example, methyl-, ethyl-,
n-propyl-, i-propyl-, butyl-

20

n = 1 - 20

(b) Organosilanes of the type $\text{R}'_x(\text{RO})_y\text{Si}(\text{C}_n\text{H}_{2n+1})$

R = alkyl, such as, for example, methyl-, ethyl-,
n-propyl-, i-propyl-, butyl-

25

R' = alkyl, such as, for example, methyl-, ethyl-,
n-propyl-, i-propyl-, butyl-

n = 1 - 20

x+y = 3

x = 1, 2

30

y = 1, 2

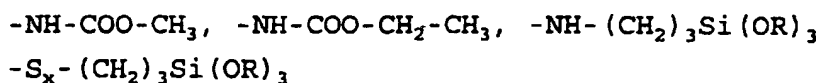
(c) Halogenorganosilanes of the type $\text{X}_3\text{Si}(\text{C}_n\text{H}_{2n+1})$

X = Cl, Br

n = 1 - 20

35

- (d) Halogenorganosilanes of the type $X_2(R')Si(C_nH_{2n+1})$
 $X = Cl, Br$
 $R' = \text{alkyl, such as, for example, methyl-, ethyl-,}$
 $\text{n-propyl-, i-propyl-, butyl-}$
5 $n = 1 - 20$
- (e) Halogenorganosilanes of the type $X(R')_2Si(C_nH_{2n+1})$
 $X = Cl, Br$
 $R' = \text{alkyl, such as, for example, methyl-, ethyl-,}$
10 $\text{n-propyl-, i-propyl-, butyl-}$
 $n = 1 - 20$
- (f) Organosilanes of the type $(RO)_3Si(CH_2)_m-R'$
 $R = \text{alkyl, such as methyl-, ethyl-, propyl-}$
15 $m = 0, 1 - 20$
 $R' = \text{methyl-, aryl (e.g. } -C_6H_5, \text{ substituted phenyl}$
 radicals)
 $-C_4F_9, OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
20 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-\underline{N-CO-(CH_2)_5}$
 $-NH-COO-CH_3, -NH-COO-CH_2-CH_3, -NH-(CH_2)_3Si(OR)_3$
 $-S_x-(CH_2)_3Si(OR)_3$
25
- (g) Organosilanes of the type $(R'')_x(RO)_ySi(CH_2)_m-R'$
 $R'' = \text{alkyl} \quad x+y = 2$
 $x = 1, 2$
 $y = 1, 2$
30 $m = 0, 1 \text{ to } 20$
 $R' = \text{methyl-, aryl (e.g. } -C_6H_5, \text{ substituted phenyl}$
 radicals)
 $-C_4F_9, -OCF_2-CHF-CF_3, -C_6F_{13}, -O-CF_2-CHF_2$
 $-NH_2, -N_3, -SCN, -CH=CH_2,$
35 $-OOC(CH_3)C = CH_2$
 $-OCH_2-CH(O)CH_2$
 $-NH-CO-\underline{N-CO-(CH_2)_5}$



(h) Halogenorganosilanes of the type $\text{X}_3\text{Si}(\text{CH}_2)_m-\text{R}'$

5 $\text{X} = \text{Cl}, \text{Br}$

$m = 0, 1 - 20$

$\text{R}' = \text{methyl-}, \text{aryl (e.g. } -\text{C}_6\text{H}_5, \text{ substituted phenyl radicals)}$

$\text{C}_4\text{F}_9, -\text{OCF}_2-\text{CHF}-\text{CF}_3, -\text{C}_6\text{F}_{13}, -\text{O}-\text{CF}_2-\text{CHF}_2$

10 $-\text{NH}_2, -\text{N}_3, -\text{SCN}, -\text{CH}=\text{CH}_2,$

$-\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$

$-\text{OCH}_2-\text{CH}(\text{O})\text{CH}_2$

$-\text{NH}-\text{CO}-\text{N}-\text{CO}-\text{(CH}_2)_5$

$-\text{NH}-\text{COO}-\text{CH}_3, -\text{NH}-\text{COO}-\text{CH}_2-\text{CH}_3, -\text{NH}-(\text{CH}_2)_3\text{Si}(\text{OR})_3$

15 $-\text{S}_x-(\text{CH}_2)_3\text{Si}(\text{OR})_3$

(i) Halogenorganosilanes of the type $(\text{R})\text{X}_2\text{Si}(\text{CH}_2)_m-\text{R}'$

$\text{X} = \text{Cl}, \text{Br}$

$\text{R} = \text{alkyl, such as methyl-}, \text{ethyl-}, \text{propyl-}$

20 $m = 0, 1 - 20$

$\text{R}' = \text{methyl-}, \text{aryl (e.g. } -\text{C}_6\text{H}_5, \text{ substituted phenyl radicals)}$

$-\text{C}_4\text{F}_9, -\text{OCF}_2-\text{CHF}-\text{CF}_3, -\text{C}_6\text{F}_{13}, -\text{O}-\text{CF}_2-\text{CHF}_2$

$-\text{NH}_2, -\text{N}_3, -\text{SCN}, -\text{CH}=\text{CH}_2,$

25 $-\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$

$-\text{OCH}_2-\text{CH}(\text{O})\text{CH}_2$

$-\text{NH}-\text{CO}-\text{N}-\text{CO}-\text{(CH}_2)_5$

$-\text{NH}-\text{COO}-\text{CH}_3, -\text{NH}-\text{COO}-\text{CH}_2-\text{CH}_3, -\text{NH}-(\text{CH}_2)_3\text{Si}(\text{OR})_3,$

where R may be = methyl-, ethyl-, propyl-, butyl-

30 $-\text{S}_x-(\text{CH}_2)_3\text{Si}(\text{OR})_3,$ where R may be = methyl-,

ethyl-, propyl-, butyl-

(j) Halogenorganosilanes of the type $(\text{R})_2\text{X Si}(\text{CH}_2)_m-\text{R}'$

$\text{X} = \text{Cl}, \text{Br}$

35 $\text{R} = \text{alkyl}$

$m = 0, 1 - 20$

$R' =$ methyl-, aryl (e.g. $-C_6H_5$, substituted phenyl radicals)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,

5 $-OOC(CH_3)C=CH_2$

$-OCH_2-CH(O)CH_2$

$-NH-CO-N-CO-(CH_2)_5$

$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$

$-S_x-(CH_2)_3Si(OR)_3$

10

(k) Silazanes of the type $R'_2R_2Si-N-SiR_2R'$

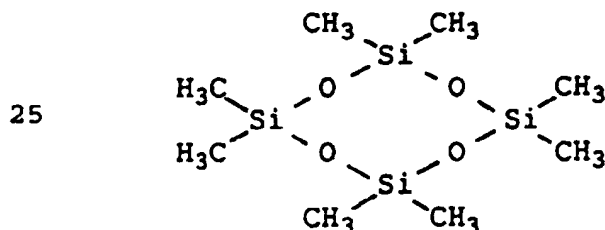


$R =$ alkyl,

15 $R' =$ alkyl, vinyl

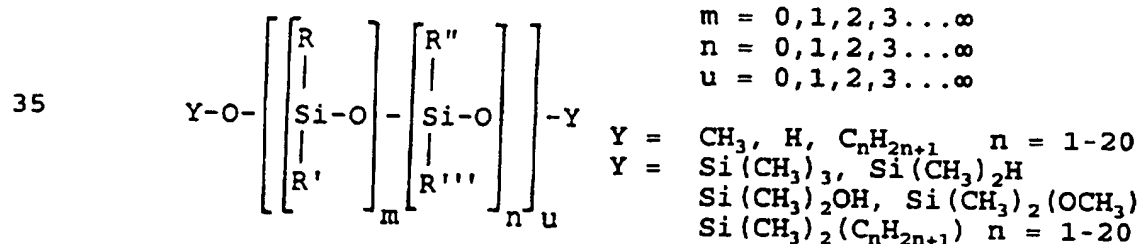
(l) Cyclic polysiloxanes of the type D 3, D 4, D 5, where D 3, D 4 and D 5 mean cyclic polysiloxanes with 3, 4 or 5 units of the type $-O-Si(CH_3)_2-$.

20 For example, octamethylcyclotetrasiloxane = D 4



30

(m) Polysiloxanes and silicone oils of the type



- R = alkyl, such as C_nH_{2n+1} , where n is = 1 to 20, aryl, such as phenyl- and substituted phenyl radicals, $(CH_2)_n-NH_2$, H
- 5 R' = alkyl, such as C_nH_{2n+1} , where n is = 1 to 20, aryl, such as phenyl- and substituted phenyl radicals, $(CH_2)_n-NH_2$, H
- R'' = alkyl, such as C_nH_{2n+1} , where n is = 1 to 20, aryl, such as phenyl- and substituted phenyl radicals, $(CH_2)_n-NH_2$, H
- 10 R''' = alkyl, such as C_nH_{2n+1} , where n is = 1 to 20, aryl, such as phenyl- and substituted phenyl radicals, $(CH_2)_n-NH_2$, H

The invention also provides a process for the preparation of

15 the surface-modified, pyrogenically produced mixed oxides according to the invention, which is characterised in that two or more metal chlorides from the series comprising $SiCl_4$, $AlCl_3$, $TiCl_4$, $ZrCl_4$, $FeCl_3$, $NbCl_5$, $VOCl_3$, $WOCl_4$, WCl_6 , $SnCl_4$ and $GeCl_4$, are evaporated together or separately,

20 transferred together with an inert gas, for example, nitrogen, into the mixing chamber of a known burner, mixed there with hydrogen, air and/or oxygen, the multi-component mixture is burned in a reaction chamber, the solid mixed oxides are then separated from the gaseous reaction products

25 and freed from adhering hydrogen chloride optionally in moist air, and the pyrogenically produced mixed oxides are charged to a suitable mixing vessel, the mixed oxides are sprayed, with intensive mixing, optionally initially with water and subsequently with the surface-modifying reagent or

30 the mixture of several surface-modifying reagents, mixed again for 15 to 30 minutes and subsequently heat-treated at a temperature of 100 to 400°C for a period of 1 to 6 hours.

The water used may be acidified with an acid, for example,

35 hydrochloric acid, to a pH of 7 to 1. The surface-modifying reagent used may be dissolved in a suitable solvent such as, for example, ethanol. The mixing and/or heat treatment may

be carried out in a protective gas atmosphere such as, for example, nitrogen.

The invention also provides a process for the preparation of the surface-modified, pyrogenically produced mixed oxides according to the invention, which is characterised in that two or more metal chlorides from the series comprising SiCl_4 , AlCl_3 , TiCl_4 , ZrCl_4 , FeCl_3 , NbCl_5 , VOCl_3 , WOCl_4 , WCl_6 , SnCl_4 and GeCl_4 are evaporated together or separately, transferred together with an inert gas, for example, nitrogen, into the mixing chamber of a known burner, mixed there with hydrogen, air and/or oxygen, the multi-component mixture is burned in a reaction chamber, the solid mixed oxides are then separated from the gaseous reaction products and freed from adhering hydrogen chloride optionally in moist air, and mixed as homogeneously as possible with organohalogen silanes with the exclusion of oxygen, the mixture together with small quantities of water vapour and optionally together with an inert gas is heated to temperatures from 200 to 800°C, preferably 400 to 600°C, in the continuous co-current process in a treatment chamber taking the form of an upright tubular furnace, the solid and gaseous reaction products are separated from each other, the solid products are optionally de-acidified and dried.

25

The invention also provides for the use of the surface-modified, pyrogenically produced mixed oxide according to the invention as

- reinforcing filler in silicone rubber and rubber
- 30 - charge stabiliser and free-flow agent in toner powders
- free-flow agent
- anti-blocking agent, for example, in films
- UV blocker, for example, in cosmetics
- thickener, for example, in lacquers.

35

Examples

Examples for the preparation of mixed oxides

- 5 The metal chlorides 1 and 2 are volatilised in separate evaporators and the chloride vapours are fed into the mixing chamber of a burner by means of nitrogen. There they are mixed with hydrogen and dried air and/or oxygen and burned in a reaction chamber. In the coagulation zone the reaction products are cooled to approximately 110°C and the resulting mixed oxides are subsequently separated with a filter. Adhering chloride is removed by treating the powders with moist air at temperatures between 500 and 700°C.
- 10
- 15 The reaction conditions and the product properties for the various mixed oxides are summarised in Table 1.

Examples for the preparation of surface-modified mixed oxides

20

The reaction conditions and stoichiometric conditions for the surface modification may be derived from Table 2. The physical-chemical data are summarised in Table 3.

Table 1: Reaction conditions and product properties of some mixed oxides

Mixed oxide example	Oxide 1 (wt.%)	Oxide 2 (wt.%)	Metal chloride 1 (g/h)	Metal chloride 2 (g/h)	H ₂ (l/h)	Air (l/h)	BET (m ² /g)	Tamped density (g/l)	Loss on ignition (%)	Chloride content (%)
1	SiO ₂ 7.5	TiO ₂ 92.5	SiCl ₄ 50	TiCl ₄ 516	470	3280	95	85	0.6	0.1
2	Al ₂ O ₃ 15	SiO ₂ 85	AlCl ₃ 126	SiCl ₄ 778	300	1300	179	104	2.9	0.12
3	Fe ₂ O ₃ 2	TiO ₂ 98	FeCl ₃ 29	TiCl ₄ 1697	525	3079	53	175	1.2	0.3
4	Fe ₂ O ₃ 7	TiO ₂ 93	FeCl ₃ 107	TiCl ₄ 1613	525	3079	46	185	1.7	0.4
5	SiO ₂ 87	ZrO ₂ 13	SiCl ₄ 1303	ZrCl ₄ 135	800	2420	121	48	0.9	0.24
6	Al ₂ O ₃ 11	TiO ₂ 89	AlCl ₃ 188	TiCl ₄ 793	448	1276	47	329	0.7	0.16
7	Al ₂ O ₃ 25	TiO ₂ 75	AlCl ₃ 464	TiCl ₄ 1269	525	3579	72	120	1.1	0.6
8	TiO ₂ 95	ZrO ₂ 5	TiCl ₄ 1661	ZrCl ₄ 78	525	3080	59	218	0.9	0.15

Table 2

E.g.	Name	Mixed oxide	Modifying reagent*	Modifying reagent (g/100g mixed oxide)	Water quantity (g/100g mixed oxide)	Solvent quantity (g/100 g mixed oxide)	Tempering time (h)	Tempering temperature (°C)
9	VT772	4	1	10	0	0	4	140
10	VT773	4	2	10	0	0	2	120
11	VT774	4	3	10	0	0	2.5	250
12	VT816	3	1	10	0	0	3	180
13	VT817	3	2	10	0	0	2	120
14	VT818	3	3	10	0	0	2.5	250
15	VT775	2	1	20	0	0	4	140
16	VT776	2	2	16	0	0	2	120
17	VT777	2	3	15	0	0	2	250
18	VT819	8	1	10	0	0	4	180
19	VT820	8	2	10	0	0	2	120
20	VT821	8	3	10	0	0	2.5	250
21	VT900	4	2	12	5	0	2.5	140
22	VT901	3	2	10	0	10**	2.5	140
23	VT747	6	2	5	0	0	2	120
24	VT748	6	2	10	0	0	2	120
25	VT749	6	4	10	0	0	2	120
26	VT750	7	2	10	0	0	2	120
27	VT751	7	4	10	0	0	2	120
28	VT719	5	1	10	5	0	3	130
29	VT734	1	3	10	0	0	2	250

- * 1 = Hexamethyldisilazane = $(\text{CH}_3)_3\text{Si}-\text{NH}-\text{Si}(\text{CH}_3)_3$
 2 = Trimethoxy-octyl-silane = $(\text{CH}_3\text{O})_3\text{Si}-(\text{CH}_2)_7-\text{CH}_3$
 3 = Dimethylpolysiloxane = $\text{HO}-\left(\begin{array}{c} \text{CH}_3 \\ | \\ \text{Si}-\text{O} \\ | \\ \text{CH}_3 \end{array}\right)_n - \text{H}$
 4 = Trimethoxy-propyl-silane = $(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

** = Ethanol

Table 3

Example	Name	Spec. surface area BET (m ² /g)	Tamped density (g/l)	Loss on drying (%)	Loss on ignition (%)	pH	Carbon content (%)
9	VT772	40	269	0.0	1.3	6.4	0.5
10	VT773	36	280	0.1	4.7	3.4	3.6
11	VT774	27	301	0.2	3.9	3.4	2.7
12	VT816	45	258	0.4	1.1	7.5	0.5
13	VT817	39	288	0.7	3.9	3.4	3.5
14	VT818	32	292	0.0	3.6	3.6	2.9
15	VT775	124	127	0.5	3.4	6.6	1.7
16	VT776	111	136	1.0	9.5	4.2	5.8
17	VT777	101	136	0.9	4.7	4.2	2.9
18	VT819	51	245	0.5	0.7	9.0	0.4
19	VT820	45	275	0.0	4.4	4.0	3.6
20	VT821	35	275	0.0	2.3	4.1	2.5
21	VT900	34	275	0.1	4.9	3.5	3.9
22	VT901	38	282	0.6	4.0	3.6	3.6
23	VT747	31	396	0.2	1.7	3.7	2.0
24	VT748	23	409	0.3	4.8	4.0	3.9
25	VT749	26	402	0.3	2.3	4.1	1.8
26	VT750	56	161	0.3	16.8	3.8	3.9
27	VT751	55	162	0.2	2.7	4.1	2.0
28	VT719	60	60	0.1	1.1	6.4	1.3
29	VT734	74	114	0.5	2.5	4.2	2.5

Patent claims

1. Surface-modified, pyrogenically produced mixed oxides

which contain two or more components from the series comprising SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , Fe_2O_3 , Nb_2O_5 , V_2O_5 , WO_3 , SnO_2 , GeO_2 and were surface-modified with one or more compounds from the following groups:

- (a) Organosilanes of the type $(\text{RO})_3\text{Si}(\text{C}_n\text{H}_{2n+1})$ R = alkyl
n = 1 - 20
- (b) Organosilanes of the type $\text{R}'_x(\text{RO})_y\text{Si}(\text{C}_n\text{H}_{2n+1})$ R = alkyl
R' = alkyl
n = 1 - 20
x+y = 3
x = 1, 2
y = 1, 2
- (c) Halogenorganosilanes of the type
 $\text{X}_3\text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
n = 1 - 20
- (d) Halogenorganosilanes of the type
 $\text{X}_2(\text{R}')\text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
R' = alkyl
n = 1 - 20
- (e) Halogenorganosilanes of the type
 $\text{X}(\text{R}')_2\text{Si}(\text{C}_n\text{H}_{2n+1})$ X = Cl, Br
R' = alkyl
n = 1 - 20
- (f) Organosilanes of the type $(\text{RO})_3\text{Si}(\text{CH}_2)_m\text{-R}'$
R = alkyl,
m = 0, 1 - 20
R' = methyl-, aryl (e.g. $-\text{C}_6\text{H}_5$, substituted phenyl radicals)
 $-\text{C}_4\text{F}_9$, $\text{OCF}_2\text{-CHF-CF}_3$, $-\text{C}_6\text{F}_{11}$, $-\text{O-CF}_2\text{-CHF}_2$
 $-\text{NH}_2$, $-\text{N}_3$, $-\text{SCN}$, $-\text{CH=CH}_2$,
 $-\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$

$-\text{OCH}_2-\text{CH}(\text{O})\text{CH}_2$
 $-\text{NH}-\text{CO}-\text{N}-\text{CO}-\text{(CH}_2)_5$
 $-\text{NH}-\text{COO}-\text{CH}_3, -\text{NH}-\text{COO}-\text{CH}_2-\text{CH}_3, -\text{NH}-(\text{CH}_2)_3\text{Si}(\text{OR})_3$
 $-\text{S}_x-(\text{CH}_2)_3\text{Si}(\text{OR})_3$

(g) Organosilanes of the type $(\text{R}'')_x(\text{RO})_y\text{Si}(\text{CH}_2)_m-\text{R}'$

$\text{R}'' = \text{alkyl } x+y = 2$

$x = 1, 2$

$y = 1, 2$

$m = 0, 1 \text{ to } 20$

$\text{R}' = \text{methyl-}, \text{aryl (e.g. } -\text{C}_6\text{H}_5, \text{ substituted phenyl radicals)}$

$-\text{C}_4\text{F}_9, -\text{OCF}_2-\text{CHF}-\text{CF}_3, -\text{C}_6\text{F}_{13}, -\text{O}-\text{CF}_2-\text{CHF}_2$
 $-\text{NH}_2, -\text{N}_3, -\text{SCN}, -\text{CH}=\text{CH}_2,$
 $-\text{OOC}(\text{CH}_3)\text{C} = \text{CH}_2$
 $-\text{OCH}_2-\text{CH}(\text{O})\text{CH}_2$
 $-\text{NH}-\text{CO}-\text{N}-\text{CO}-\text{(CH}_2)_5$
 $-\text{NH}-\text{COO}-\text{CH}_3, -\text{NH}-\text{COO}-\text{CH}_2-\text{CH}_3, -\text{NH}-(\text{CH}_2)_3\text{Si}(\text{OR})_3$
 $-\text{S}_x-(\text{CH}_2)_3\text{Si}(\text{OR})_3$

(h) Halogenorganosilanes of the type $\text{X}_3\text{Si}(\text{CH}_2)_m-\text{R}'$

$\text{X} = \text{Cl}, \text{Br}$

$m = 0, 1 - 20$

$\text{R}' = \text{methyl-}, \text{aryl (e.g. } -\text{C}_6\text{H}_5, \text{ substituted phenyl radicals)}$

$-\text{C}_4\text{F}_9, -\text{OCF}_2-\text{CHF}-\text{CF}_3, -\text{C}_6\text{F}_{13}, -\text{O}-\text{CF}_2-\text{CHF}_2$
 $-\text{NH}_2, -\text{N}_3, -\text{SCN}, -\text{CH}=\text{CH}_2,$
 $-\text{OOC}(\text{CH}_3)\text{C} = \text{CH}_2$
 $-\text{OCH}_2-\text{CH}(\text{O})\text{CH}_2$
 $-\text{NH}-\text{CO}-\text{N}-\text{CO}-\text{(CH}_2)_5$
 $-\text{NH}-\text{COO}-\text{CH}_3, -\text{NH}-\text{COO}-\text{CH}_2-\text{CH}_3, -\text{NH}-(\text{CH}_2)_3\text{Si}(\text{OR})_3$
 $-\text{S}_x-(\text{CH}_2)_3\text{Si}(\text{OR})_3$

(i) Halogenorganosilanes of the type $(\text{R})\text{X}_2\text{Si}(\text{CH}_2)_m-\text{R}'$

$\text{X} = \text{Cl}, \text{Br}$

$\text{R} = \text{alkyl},$

$m = 0, 1 - 20$

$R' =$ methyl-, aryl (e.g. $-C_6H_5$, substituted phenyl radicals)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,

$-OOC(CH_3)C=CH_2$

$-OCH_2-CH(O)CH_2$

$-NH-CO-N-CO-(CH_2)_5$

$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$,

$-S_x-(CH_2)_3Si(OR)_3$

(j) Halogenorganosilanes of the type $(R)_2X Si(CH_2)_m-R'$

$X = Cl, Br$

$R =$ alkyl

$m = 0, 1 - 20$

$R' =$ methyl-, aryl (e.g. $-C_6H_5$, substituted phenyl radicals)

$-C_4F_9$, $-OCF_2-CHF-CF_3$, $-C_6F_{13}$, $-O-CF_2-CHF_2$

$-NH_2$, $-N_3$, $-SCN$, $-CH=CH_2$,

$-OOC(CH_3)C=CH_2$

$-OCH_2-CH(O)CH_2$

$-NH-CO-N-CO-(CH_2)_5$

$-NH-COO-CH_3$, $-NH-COO-CH_2-CH_3$, $-NH-(CH_2)_3Si(OR)_3$,

$-S_x-(CH_2)_3Si(OR)_3$

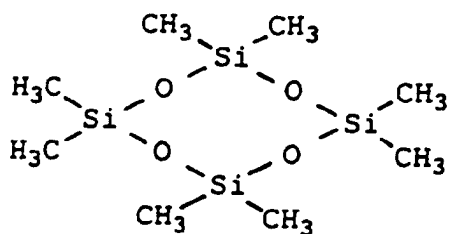
(k) Silazanes of the type $R'_2Si-N-SiR'_2$

|
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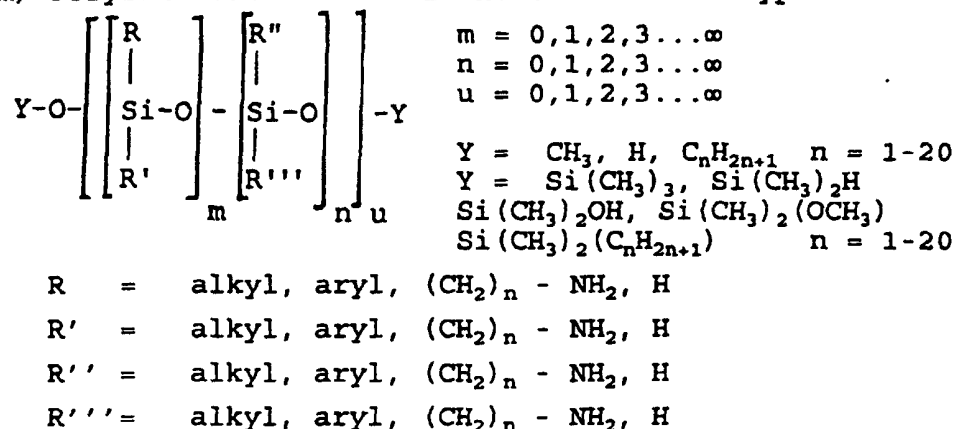
$R =$ alkyl,

$R' =$ alkyl, vinyl

(l) Cyclic polysiloxanes of the type D 3, D 4, D 5,
e.g. octamethylcyclotetrasiloxane = D 4



(m) Polysiloxanes and silicone oils of the type



2. A process for the preparation of surface-modified, pyrogenically produced mixed oxides according to claim 1, characterised in that two or more metal chlorides from the series comprising $SiCl_4$, $AlCl_3$, $TiCl_4$, $ZrCl_4$, $FeCl_3$, $NbCl_5$, $VOCl_3$, $WOCl_4$, WCl_6 , $SnCl_4$ and $GeCl_4$, are evaporated together or separately, transferred together with an inert gas, for example, nitrogen, into the mixing chamber of a known burner, mixed there with hydrogen, air and/or oxygen, the multi-component mixture is burned in a reaction chamber, the solid mixed oxides are then separated from the gaseous reaction products and freed from adhering hydrogen chloride optionally in moist air, and the pyrogenically produced mixed oxides are charged to a suitable mixing vessel, the mixed oxides are sprayed, with intensive mixing, optionally initially with water and subsequently with the surface-modifying reagent or the mixture of several surface-modifying reagents, mixed again for 15 to 30 minutes and subsequently heat-treated at a temperature of 100 to 400°C for a period of 1 to 6 hours.
3. A process for the preparation of surface-modified, pyrogenically produced mixed oxides according to claim 1, characterised in that two or more metal chlorides from the series comprising $SiCl_4$, $AlCl_3$, $TiCl_4$, $ZrCl_4$, $FeCl_3$, $NbCl_5$, $VOCl_3$, $WOCl_4$, WCl_6 , $SnCl_4$ and $GeCl_4$ are evaporated together

or separately, transferred together with an inert gas, for example, nitrogen, into the mixing chamber of a known burner, mixed there with hydrogen, air and/or oxygen, the multi-component mixture is burned in a reaction chamber, the solid mixed oxides are then separated from the gaseous reaction products and freed from adhering hydrogen chloride optionally in moist air, and mixed as homogeneously as possible with organohalogen silanes with the exclusion of oxygen, and the mixture together with small quantities of water vapour and optionally together with an inert gas is heated to temperatures from 200 to 800°C, preferably 400 to 600°C, in the continuous co-current process in a treatment chamber taking the form of an upright tubular furnace, the solid and gaseous reaction products are separated from each other, the solid products are optionally de-acidified and dried.

4. The use of the surface-modified, pyrogenically produced mixed oxide according to claim 1 as
 - reinforcing filler in silicone rubber and rubber
 - charge stabiliser and free-flow agent in toner powders
 - free-flow agent
 - anti-blocking agent, for example, in films
 - UV blocker, for example, in cosmetics
 - thickener, for example, in lacquers.
5. Surface modified, pyrogenically produced mixed oxides substantially as hereinbefore described with particular reference to the examples.
6. A process for the production of surface modified, pyrogenically produced mixed oxides substantially as hereinbefore described with particular reference to the examples.



Application No: GB 9600301.7
Claims searched: 1-6

Examiner: C.A. Clarke
Date of search: 11 March 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C1A (AVF1,AVF3)

Int CI (Ed.6): C09C 3/12

Other:

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2056995 A DEGUSSA see claim1 and p2 line 11-12	1
X	GB 1592802 UNION CARBIDE see p9 lines 22-42	1
X	GB 1371219 DEUTSCHE GOLD UND SILBER see Example 8	1
X	GB 1371218 DEUTSCHE GOLD UND SILBER see example 2	1
X	EP 0417866 A SHISEIDO see p9 line 55 - p10 line 7	1
X	EP 0212870 A SHISEIDO see p26 lines 11-28	1

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

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A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.

E Patent document published on or after, but with priority date earlier than, the filing date of this application.